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Partial Specific Compressibility and Its Relation to Solvation of Solute Based on Measurements of Suspension System

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The relation between limiting partial specific compressibility, $\bar{\kappa}_2{}^0$, and solvation of solute was reviewed and determination of $\bar{\kappa}_2{}^0$ was carried out in different types of solutions; ideal binary mixtures, such as benzene–toluene, and suspension systems of polystyrene latex and colloidal silica. In ideal mixture and polystyrene latex systems, the partial specific compressibility and limiting partial specific volume of each solute were equal to the corresponding value of the solute itself. The $\bar{\kappa}_2{}^0$ of the colloidal silica decreased from a positive to negative value with increasing pH of the media, showing strong hydration in alkaline solution.

In the last two decades compressibility measurement of solution has become quite familiar to many workers who are interested in solute–solvent interaction. Increase of attention to the compressibility in solution chemistry is ascribed to the appearance of commercial apparatus for ultrasonic velocity measurement and also to the development of molecular dynamical study of solution stimulated by computer simulation and various experimental techniques. As is well-known, the compressibility of solution is related to the radial distribution function of the molecules composing solutions.[1)]

It goes without mentioning here the important role played by compressibility measurements in the estimation of amount of hydration of electrolytes which go back to the pioneering work of Passynski done as early as in 1938.[2)] In his treatment, Passynski assumed that the compressibility of ionic solute and water molecules hydrated to the solute be incompressible. This hydration model, though simplified, is reasonable, since solvent molecules around ionic solute are subject to very strong electric field, namely they are electrostricted and their compressibility should be very small in comparison with that of bulk solvent.

On the other hand, for more general discussion of solute–solvent interaction from the point of solution compressibility, Nomura and Miyahara,[3)] using a realistic model of solvated polymer molecule in solution, defined the limiting partial specific compressibility of solute, $\bar{\kappa}_2{}^0$, about twenty years ago. Since then, Miyahara and his coworkers determined the values of $\bar{\kappa}_2{}^0$ of many kinds of polymers in various conditions.[4)] The solvation model proposed by them (abbreviated as N–M solvation model) can be extended to solutes other than polymers and amounts of solvent molecules bound to the solutes were determined for such systems as dextran in water[5)] and in the mixed solvent of water–ethanol,[6)] and cyclodextrin in the same mixed solvent.[7)] Moreover, the N–M solvation model is useful in estimating the compressibility of certain kind of solute, for example polysaccharide, by means of ethanol-precipitation technique proposed originally by Shiio et al.[8)]

As will be seen later in the present paper, the relation between $\bar{\kappa}_2{}^0$ and the amount of solvation is based basically on the assumption that the solvated or hydrated molecules make ideal solution with the solvent or water. This assumption is the same as that used in determination of the amount of hydrated water for electrolytes[9)] and saccharides[10)] from respective activity data. In spite of a number of papers dealing with the parameter $\bar{\kappa}_2{}^0$ reported by Miyahara's school,[3–7)] direct experimental confirmation of the proposed relation of $\bar{\kappa}_2{}^0$ with the N–M solvation model using well-defined solute species is scare, except for one paper.[11)] Considering recent increasing attention to the solution compressibility and importance of the information deduced therefrom, we found it appropriate to re-examine at this time the relation between the parameter $\bar{\kappa}_2{}^0$ and compressibility of solute in a more rigorous way. For this purpose we have undertaken the measurements of compressibility for the systems for which the compressibility of solute can be defined without any ambiguity.

The systems investigated are the ideal binary mixtures and the suspension systems. The formers are toluene–benzene, and -*m*-xylene, toluene being considered as solvent, while the latters are the solutions of monodisperse polystyrene latex and those of colloidal silica. As for the compressibility of suspension system, Urick[12)] and Fukutomi and Wada[13)] estimated the compressibility of a suspensoid from compressibility data for a dispersed phase and dispersion media.

Definition and Model

We briefly discuss compressibility of liquids and solutions and review the N–M solvation model.[3)]

Definition of the Limiting Partial Specific Compressibility. The limiting partial specific compressibility of solute, $\bar{\kappa}_2{}^0$, is defined in the following equation:[3)]

$$\bar{\kappa}_2{}^0 \equiv -\frac{1}{\bar{v}_2{}^0}\left(\frac{\partial \bar{v}_2}{\partial p}\right)_{s,0}, \tag{1}$$

where $\bar{v}_2^0$ is the limiting partial specific volume of the solute. The subscripts zero and s refer respectively to the state at infinite dilution and the isentropic condition. An alternative definition of $\bar{\kappa}_2^0$ is

$$\bar{\kappa}_2^0 \equiv \frac{1}{\bar{v}_2^0}\left(\frac{\partial \kappa}{\partial x}\right)_0 + \kappa_1, \tag{2}$$

where κ is the compressibility and x is the concentration of solute expressed in g cm^{-3} of solution. In the present paper the subscripts 1 and 2 always refer to the solvent and solute, respectively. The quantity $\bar{\kappa}_2^0$ is evaluated from extrapolation of the data of compressibility κ and density d of solution in a following way;

$$\bar{\kappa}_2^0 = -\frac{\kappa_1}{\bar{v}_2^0}\lim_{x\to 0} K_x, \tag{3}$$

$$K_x = \left(\frac{d-x}{d_1} - \frac{\kappa}{\kappa_1}\right)\frac{1}{x},$$

Compressibility concerned here is that under adiabatic condition and is obtained from the well-known Laplace equation:

$$\kappa = \frac{1}{du^2}, \tag{4}$$

u being ultrasonic velocity in the solution. The parameter K_x is related to the apparent molar adiabatic compressibility $K_{s\phi}(=-(\partial\phi_v/\partial p)_s)$ by the equation,

$$K_x = -\frac{K_{s\phi}}{\kappa_1 M}, \tag{5}$$

where M is the molar mass of the solute.

Statistical Mechanical Expression of $\bar{\kappa}_2^0$. In order to have microscopic information on the solute–solvent interaction from the data of compressibility of solution, a statistical mechanical expression of $\bar{\kappa}_2^0$ is earnestly required. However, to derive statistical mechanical expression is a very hard task, since compressibility is directly related to the volume of the system under considerations. The only one theory available and based on the statistical mechanical treatment is the theory proposed by Kirkwood and Buff.1) Using their theory, the limiting partial specific compressibility can be expressed as follows:

$$(\kappa_{2,T}^0 - \kappa_{1,T}) = \frac{1}{\bar{v}_2^0}[G_{112}^0 - G_{111}^0 + G_{11}^{0\,2} - G_{12}^{0\,2}]$$

$$-\frac{v_1}{\bar{v}_2^0}[G_{11}^0 - G_{12}^0], \tag{6}$$

$$G_{ij}^0 = \int [g_{ij}^{(2)0}(r_{ij}) - 1]\mathrm{d}v, \tag{7}$$

$$G_{ijk}^0 = \iint [g_{ijk}^{(3)0}(r_{12}, r_{13}) - g_{ij}^{(2)0}(r_{12}) - g_{ik}^{(2)0}(r_{13}) - g_{jk}^{(2)0}(r_{23}) + 2]\mathrm{d}v_{12}\mathrm{d}v_{13}, \tag{8}$$

where the suffix T is used to refer to an isothermal condition and $g_{ij}^{(2)}(r_{ij})$ and $g_{ijk}^{(3)}(r_{ij},r_{jk})$ are respectively the pair and triple distribution function in binary solution system. Comparison of Eqs. 6 and 2 shows what kind of information we can deduce from the values of $\bar{\kappa}_2^0$. The terms $[G_{112}^0 - G_{111}^0]$ and $[G_{11}^0 - G_{12}^0]$ are closely related to the solvation of solute and they can be estimated from the experimental data. Unfortunately, at present, we can not go any further into discussion of compressibility on molecular level starting from the values of the $[G_{112}^0 - G_{111}^0]$ and $[G_{11}^0 - G_{12}^0]$ terms. We, therefore, ought to rely upon a proper model in order to discuss the solute-solvent interaction in terms of compressibility data.

$\bar{\kappa}_2^0$ and the N-M Solvation Model. The proposed N-M solvation model is schematically represented in our previous paper.3) In this model, we have assumed that the solvated or hydrated molecules make ideal solution with the solvent or water, and the so-called structure breaking region in the Frank-Wen model14) is wholly ignored. If the volume additivity holds even after solvation for such solvated molecules in solution, then the total volume of solution V is given by

$$V = (n_1 - n_s n_2)v_1 + n_2(v_2 + n_s v_s), \tag{9}$$

where v_1, v_2, and v_s are the specific volume of the bulk solvent, solute and solvent in the solvation region, and n_s is the gram number of solvent in the solvation region per one gram of solute. In dilute solution, we may consider the n_s to be independent of the concentration of solute.

The partial specific volume of the solute is given by the differentiation of V with respect to solute concentration:

$$\bar{v}_2 = \left(\frac{\partial V}{\partial n_2}\right)_{n_1} = v_2 + n_s(v_s - v_1). \tag{10}$$

On taking the pressure derivative of Eq. 9 under the condition of constant entropy, we obtain the following relation according to the definition of $\bar{\kappa}_2^0$ shown in Eq. 1:

$$\bar{\kappa}_2^0 = \frac{v_2}{\bar{v}_2^0}\kappa_2 + \frac{n_s}{\bar{v}_2^0}(v_s\kappa_s - v_1\kappa_1). \tag{11}$$

If the solution concerned behaves non-ideally but so long as the volume contraction due to the solvation is negligible in order of magnitude, we can assume the relation below:

$$v_s \simeq v_1 \quad \text{and} \quad \bar{v}_2^0 \simeq v_2. \tag{12}$$

Equation 11 can then be written as

$$\bar{\kappa}_2^0 = \kappa_2 + \frac{n_s v_1}{\bar{v}_2^0}(\kappa_s - \kappa_1). \tag{13}$$

In case where no solvation occurs; i.e. $n_s=0$ and/or $\kappa_s=\kappa_1$. Equation 13 is reduced to an equation

$$\bar{\kappa}_2^0 = \kappa_2. \tag{14}$$

In more general cases in which the compressibility of solvation layer κ_s is taken into account, the amount of solvation can be calculated as follows:

$$v_1 n_s = \bar{v}_2{}^0 \frac{\bar{\kappa}_2{}^0 - \kappa_2}{\kappa_s - \kappa_1}. \tag{15}$$

For electrolytic solutes in solution, especially in aqueous solution, we can safely assume $\kappa_2=0$ and $\kappa_s=0$, as done by Passynski.[2] Then, we have from Eqs. 3 and 15

$$n_s = \frac{1}{v_1} \lim_{x\to 0} K_x. \tag{16}$$

If Eq. 9 is directly differentiated with respect to pressure and both quantities κ_2 and κ_s are assumed to be zero, as for the case of electrolytic solute, we have

$$n_s = \frac{n_1}{n_2}\left(1 - \frac{\kappa}{\kappa_1}\frac{V}{n_1 v_1}\right). \tag{17}$$

This equation is essentially the same as that proposed by Passynski.[2]

If the N-M solvation model is applied to the liquid–liquid mixtures where solute molecules interact negligibly with the surrounding solvent, the $\bar{\kappa}_2{}^0$ values should agree with the adiabatic compressibility of the solute itself in pure liquid state. Moreover, in ideal suspension system, the relation 14 should hold. As the adiabatic compressibility and specific volume of the suspensoid in solid state are defined and evaluated unequivocally, comparisons of the $\bar{\kappa}_2{}^0$ with κ_2 and $\bar{v}_2{}^0$ with v_2 are highly meaningful.

Experimental

Samples. Sample liquids *m*-xylene, benzene, and toluene used were all commercial products, spectral grade, of Nakarai Chemicals Co., Ltd. and they were used after purification by fractional distillation. Polystyrene latexes used were courteously supplied from Nippon Synthetic Rubber Co., Ltd. and their diameters were determined by the dynamic light scattering method using a spectrometer Coulter Model N4 as to be 246 (monodisperse), 123 (monodisperse), and 84±20 nm. The ζ-potentials, which serve as a measure of surface charge density, fall between −66 and −74 mV for the three latex samples mentioned above. The values were determined by a ζ-potentiometer Pen KEW 3000.

The colloidal silicas used in this work are commercial products Snowtex S, 20, and 20L supplied from Nissan Chemicals Co., Ltd. Particle size distribution was determined from the photographs taken by an electron microscope. The mean diameter of the sample Snowtexes are 8.1±2.9, 14.6±4.4, and 42.7±15.0 nm, respectively.

Measurements. The adiabatic compressibility of the sample solutions were determined from the measurements of ultrasonic velocities and densities of solutions. The former measurements were carried out using an ultrasonic interferometer operating at constant frequency of 5.000008 MHz, while the latters were done by means of a conventional Ostwald pycnometer of 20 cm³. The procedure of sound velocity measurement and its accuracy is described in details elsewhere.[15]

Preparation of Sample Solutions. The original commercial products of colloidal silica Snowtex have the pH values about 10. Adjustment of the pH of colloidal silica solution was attained in two steps; first, making the colloidal silica pass through the ion-exchange resin (mixed bed, Amberlite IRA-400 and IR-120), then adding small quantity of solutions of HCl to raise the pH of colloidal silica solution to a desired pH value. The ion-exchanged colloidal solution has the pH values equal to 2—3 and this pH region corresponds to the isoelectric point of the colloidal silica.[16] Colloidal silica is unstable in the neutral pH region and if the solution is kept standing in the neutral pH region for one night, then the colloidal silica shows gelation. Therefore, measurements are difficult in the pH ranges 5—7.

Content of silica and polystyrene latexes in each colloidal solution and suspension was determined from the weight of solid residue left after drying the sample solution.

All measurements were carried out at 25 °C.

Results and Discussion

To illustrate the accuracy of extrapolation and also to confirm our assumptions, $(d-x)/d_1$, and κ/κ_1 are plotted against x for the typical examples of ideal

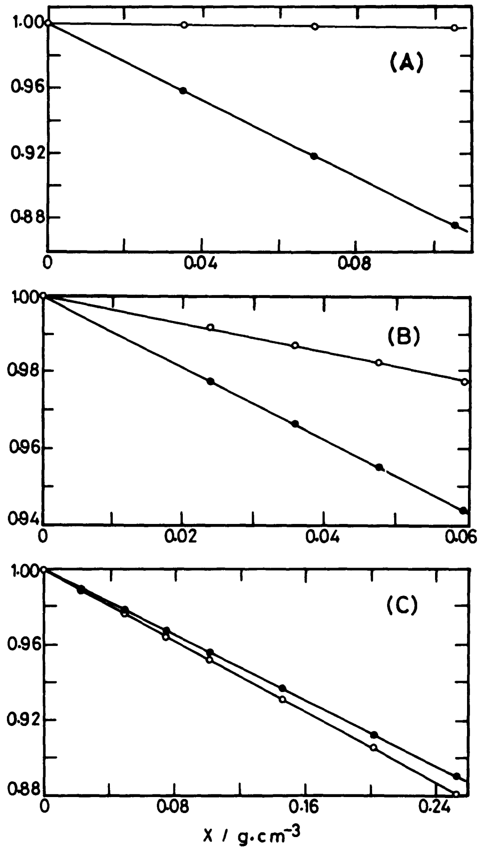

Fig. 1. $(d-x)/d_1$ and κ/κ_1 plotted against concentration X; ● $(d-x)/d_1$, ○ k/k_1.
A: *m*-xylene–toluene, B: polystyrene latex with diameter 84 nm, C: Snowtex S at pH 10.50.

binary mixtures of *m*-xylene–toluene, suspension of polystyrene latexes and silica sol, respectively in Fig. 1. As is seen in Fig. 1, linear relations were observed for both quantities in the concentration ranges investigated, that is, the value of K_x is independent of concentration. The limiting value of K_x was estimated from the slopes of these two lines. Values of $\bar{\kappa}_2^0$ are obtained by Eq. 3.

Values of $\bar{\kappa}_2^0$ in the Ideal Mixture. It is well-known that benzene, *m*-xylene, and styrene form ideal solution with toluene. In Table 1, the values of $\bar{\kappa}_2^0$ and $\bar{v}_2^0$ are compared respectively with κ_2 and v_2 for the solutes benzene, *m*-xylene, and styrene dissolved in toluene. As is seen Table 1, the relations $\bar{v}_2^0=v_2$ and $\bar{\kappa}_2^0=\kappa_2$ hold obviously, as predicted from Eqs. 12 and 14 for these systems. Consequently, in these mixtures no specific interactions are working between solute and solvent molecules.

Values of $\bar{\kappa}_2^0$ of Suspensoids. The results obtained from the ultrasonic velocity and density measurements of suspensions of various monodisperse polystyrene latexes are summarized in Table 2.

Although the values are scattering to some extent, the average values of $\bar{v}_2^0$ and $\bar{\kappa}_2^0$ are 0.941 cm^3 g^{-1} and 25.3×10^{-11} Pa^{-1}, respectively. The specific volume and compressibility of solid polystyrene are 0.953 and 24×10^{-11}, respectively at 20 °C in the same unit as above.[17] Therefore, the relation expressed as Eqs. 12 and 14 are retained in the suspension system in which particle diameters of suspensoid are ranging from 84 to 400 nm. It may be expressed that the smaller the diameter of suspensoid particle, the larger will be the surface effects in the values of $\bar{\kappa}_2^0$ which reflect the interaction between the surface of the particle and solvent molecules. However, down to the diameter 80 nm of the suspensoid, no appreciable surface effect was observed.

Values of $\bar{\kappa}_2^0$ and $\bar{v}_2^0$ of the Colloidal Silica Samples. The limiting partial specific compressibilities of electrolytes in aqueous solutions are mostly negative, for example, $\bar{\kappa}_2^0$(KCl)=−162×10^{-11} Pa^{-1} at 25 °C. This corresponds to hydration arising from very strong electrostrictive force. The colloidal silica is a sort of sols. It is stabilized by the electric repulsive force acting among colloidal particles and at the same time contributing to the formation of hydration layer around the particles. The colloidal silica can be taken as a model system of large hard sphere solute placed in a homogenious media.

The pH dependences of $\bar{\kappa}_2^0$ and $\bar{v}_2^0$ of colloidal silica sols are shown in Figs. 2 and 3, respectively. In these figures both quantities decrease with increasing pH value of the media. As will be seen below, these observations are interpreted in terms of the strong

Table 1. Comparison of the Values of $\bar{\kappa}_2^0$ and $\bar{v}_2^0$ in Toluene with the Compressibility Values in Pure State at 25 °C

	v_2 cm^3 g^{-1}	$\bar{v}_2^0$ cm^3 g^{-1}	κ_2 Pa^{-1}	$\bar{\kappa}_2^0$ Pa^{-1}
Benzene	1.150	1.145±0.001	67.69	68.70±0.06
m-Xylene	1.163	1.163±0.002	66.73	67.21±0.01
Styrene[a]	1.120	1.119±0.001	61.30	58.94±0.05

a) Ref. 11 (at 34 °C).

Table 2. Values of $\bar{\kappa}_2^0$ and $\bar{v}_2^0$ for Various Polystyrene Latexes Dispersed in Water at 25 °C

Diameter nm	$\bar{v}_2^0$ cm^3 g^{-1}	$\bar{\kappa}_2^0$×10^{11} Pa^{-1}
400[a]	0.961±0.07[a),b)]	26.8±0.6
246	0.919±0.006	21.4±0.7
123	0.941±0.008	25.2±1.7
84	0.941±0.001	27.6±0.6

a) Ref. 6. b) On p. 251 of Ref. 6, the value 0.691 is given as $\bar{v}_2^0$, which should be corrected as this value.

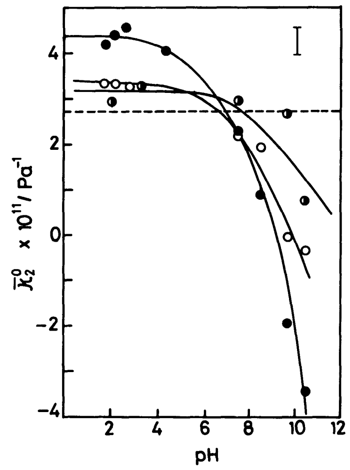

Fig. 2. Variation of $\bar{\kappa}_2^0$ of silica particle with pH of the media at 25 °C. The broken line refers to the κ_2 of quartz. The vertical bar indicates the preciseness of each measurement.
●: Snowtex S, ○: Snowtex 20, ◑: Snowtex 20L.

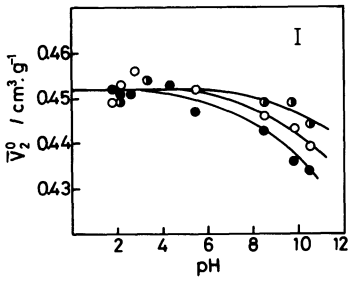

Fig. 3. Variation of $\bar{v}_2^0$ of silica particle with pH of the media at 25 °C. The vertical bar indicates the preciseness of each measurement.
●: Snowtex S, ○: Snowtex 20, ◑: Snowtex 20L.

hydration in alkaline region.

A number of silanol radicals -SiOH are distributed on the surface of colloidal silica particles and these silanol radicals are dissociated to a degree following the pH of the media. The silanol radical works similarly as an amphoteric electrolyte and its isoelectric point lies around pH 2. Therefore, in the higher pH region, the surface of the colloidal silica is charged positively like a cation. Somewhat different behaviors are observed in Figs. 2 and 3, depending on the particle size; in alkaline pH region the values of $\bar{\kappa}_2^0$ and $\bar{v}_2^0$ become smaller with decreasing particle size. However, in this work no examination was attempted to measure the surface charge density of each colloidal silica particle, as mentioned in the preceding chapter. At present it seems legitimate to postpone the detailed discussion concerning the particle size dependence until we have sufficient knowledge on this subject.

Following values[18] have been given for the values of κ_2 and v_2 of silica in bulk state at 25 °C.

$$\kappa_2 = 2.70 \times 10^{-11}\ \mathrm{Pa^{-1}} \text{ and } v_2 = 0.543\ \mathrm{cm^3\ g^{-1}}$$

In Fig. 3, the values of $\bar{v}_2^0$ in low pH region are close to the above mentioned specific volume of solid quartz. The fact that $\bar{v}_2^0 = v_2$ is equivalent to set $n_s=0$ in Eq. 10.

This means that colloidal silica is not hydrated in acidic pH region. On the contrary, decrease of $\bar{v}_2^0$ with pH of the colloidal system suggests that $v_1 > v_s$ in Eq. 10 and that the term n_s increases with the pH value.

In correspondence to Fig. 3, the values of $\bar{\kappa}_2^0$ in acidic region are positive and a little larger than the compressibility of fused quartz as illustrated in Fig. 2, while they decrease to be negative in alkaline solutions. These variations correspond to $v_s\kappa_s < v_1\kappa_1$ in Eq. 11 or 13. As described just above, the relation $v_s < v_1$ holds. Therefore, the water molecules in hydration layer seem to be less compressible than those in bulk phase. In alkaline region where the relations $\bar{\kappa}_2^0 < \kappa_2$ and $\bar{v}_2^0 < v_2$ are observed, colloidal silica particles are doubtlessly hydrated. Evaluation of the parameters n_s and v_s is possible on solving simultaneously Eqs. 10 and 11. In doing so, a proper value must be assumed for the value of κ_s. The two cases were considered; $\kappa_s=0$ and $\kappa_s=11.1 \times 10^{-11}\ \mathrm{Pa^{-1}}$. The latter refers to the compressibility of hexagonal ice. The differences $\bar{v}_2^0 - v_2$ and $\bar{\kappa}_2^0 - \kappa_2$ used in this evaluation are significant to one or at most two figures and self-consistent, i.e. reasonable both for v_s and n_s, results were obtained only for the colloidal solutions with pH >8.5. Accuracy of the evaluation prevents detailed analysis of the results given in Table 3. However, the average values of v_s seems too small in view of the size of colloidal particles and the estimated electrostriction volume of ions in water.[19,20)]

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Table 3. Amount of Water Bound on the Colloidal Silica Surface and Specific Volume of Water in Hydration Layer in Higher pH Region of the Media

Sample	pH	$\kappa_s=0$			$\kappa_s=\kappa_{\mathrm{ice}}$		
		n_s / $\mathrm{g\ g^{-1}}$	n_s' / $\mathrm{g\ g^{-1}\ cm^{-2}}$	v_s / $\mathrm{cm^3\ g^{-1}}$	n_s / $\mathrm{g\ g^{-1}}$	n_s' / $\mathrm{g\ g^{-1}\ cm^{-2}}$	v_s / $\mathrm{cm^3\ g^{-1}}$
S	9.7	4.6×10^{-2}	4.6×10^{14}	0.64	5.6×10^{-2}	5.6×10^{14}	0.70
	10.5	6.1	6.0	0.70	7.5	7.4	0.75
20	9.7	2.7	5.0	0.65	3.4	6.0	0.72
	10.5	3.0	5.5	0.55	3.6	6.5	0.62
20 L	10.5	2.0	10	0.56	2.3	12	0.63
				mean 0.62			mean 0.68

n_s' is amount of hydration per unit area of particle surface.

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